

Determining the crystal-field ground state in rare earth Heavy Fermion materials using soft-x-ray absorption spectroscopy

P. Hansmann,¹ A. Severing,¹ Z. Hu,¹ M. W. Haverkort,¹ C. F. Chang,¹ S. Klein,¹
A. Tanaka,² H. H. Hsieh,³ H.-J. Lin,⁴ C. T. Chen,⁴ B. Fåk,⁵ P. Lejay,⁶ and L. H. Tjeng¹

¹*II. Physikalisches Institut, Universität zu Köln, Zùlpicher StraÙe 77, D-50937 Köln, Germany*

²*Department of Quantum Matter, ADSM Hiroshima University, Higashi-Hiroshima 739-8530, Japan*

³*Chung Cheng Institute of Technology, National Defense University, Taoyuan 335, Taiwan*

⁴*National Synchrotron Radiation Research Center (NSRRC), 101 Hsin-Ann Road, Hsinchu 30077, Taiwan*

⁵*CEA, Département de Recherche Fondamentale sur la Matière Condensée, SPSMS, 38054, Grenoble, France*

⁶*Institut Néel, CNRS, BP 166, 38042 Grenoble Cedex 9, France*

(Dated: February 2, 2008)

We infer that soft-x-ray absorption spectroscopy is a versatile method for the determination of the crystal-field ground state symmetry of rare earth Heavy Fermion systems, complementing neutron scattering. Using realistic and universal parameters, we provide a theoretical mapping between the polarization dependence of Ce $M_{4,5}$ spectra and the charge distribution of the Ce $4f$ states. The experimental resolution can be orders of magnitude larger than the $4f$ crystal field splitting itself. To demonstrate the experimental feasibility of the method, we investigated CePd₂Si₂, thereby settling an existing disagreement about its crystal-field ground state.

PACS numbers: 71.27.+a, 75.10.Dg, 75.30.Mb, 78.70.Dm

Heavy Fermion materials are strongly correlated rare earth or actinide materials where the atomic-like f electrons interact with conduction electrons giving rise to extraordinary low energy properties. There has been a revival of interest in many of these well studied compounds with an intense search for new ones since the discovery that many of these materials are at the border between magnetic order and superconductivity when driven through a quantum critical point by either applying a magnetic field or pressure, and/or exhibit non-Fermi liquid behavior [1, 2, 3, 4, 5, 6, 7, 8, 9]. There are indications that the unconventional superconductivity in these compounds is triggered by antiferromagnetic correlations leading to the interesting aspect of competing magnetic and superconducting order parameters which may involve a momentum dependent hybridization of f and conduction electrons [10, 11, 12]. Therefore, any microscopic understanding of how the wealth of properties in Heavy Fermion materials evolves out of the strongly interacting f ground state requires the knowledge of the spatial distribution of the f state involved. It has been pointed out already early by Zwicky, for example, that the Fermi surface of several systems depends strongly on the crystal-field symmetries [13]. Other effects like the quadrupolar ordering reflect the charge distribution of the f ground state [14, 15, 16, 17], but so far reliable input from experiment is scarce.

The standard experimental technique to determine the crystal-field energy level scheme is inelastic neutron scattering on polycrystalline samples. The additional information of quasi- and inelastic intensities should be sufficient to extract information about the f spatial distribution as well, but the analysis of magnetic intensities is often hampered by broadened lines, phonons in the same

energy window as the magnetic excitations or strong absorption of one of the sample's constituents (e.g. Rh, In, B, or Sm). Therefore, the wave functions of the crystal-field states are often determined from a combined analysis of neutron and single crystal static susceptibility data [18, 19, 20]. However, as pointed out by Witte *et al.* [21] and Janoušová *et al.* [22], even this combined method often fails due to the powder and thermal averaging in either technique. Moreover, in the presence of magnetic order anisotropic molecular field parameters have to be introduced in order to fit the static susceptibility, ending up with too many free parameters for a unique description of the crystal-field potential, leaving ambiguities and unresolved debates in the present literature. One then has to resort to time consuming inelastic polarized neutron scattering experiments with their demand for large single crystals [21, 22], or, equally time consuming, to elastic scattering experiments with polarized neutrons to determine the f magnetic form factor [23]. The latter has the advantage that it is also applicable for systems in which crystal-field excitations are not defined [24]. Nevertheless, neutron based methods have their limitations in case the compound under study contains more than one type of magnetic ion.

We will show in this report at the example of CePd₂Si₂ that polarization dependent soft-x-ray absorption spectroscopy at the rare earth $M_{4,5}$ edges (soft-XAS) is a powerful tool to give undisguised direct information concerning the $4f$ charge distribution in the ground state. This technique is complementary to inelastic and elastic neutron scattering, but has the advantage of having orders of magnitude better signal-to-noise/background-ratio and of requiring only small amounts of sample material. It is capable of measuring materials which are

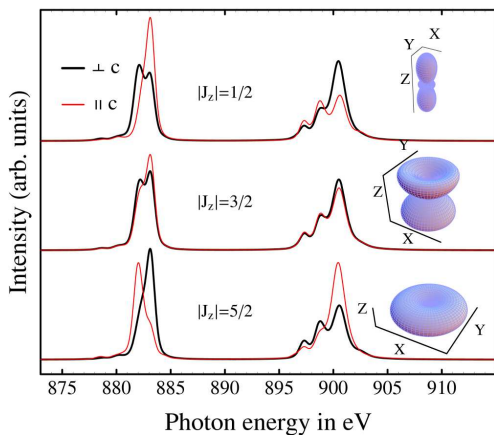


FIG. 1: (color online) Calculated $M_{4,5}$ soft-x-ray absorption spectra for pure $|J_z\rangle$ states of Ce^{3+} for the incoming light polarized \parallel and \perp \mathbf{c} ($\mathbf{z} \parallel \mathbf{c}$ in tetragonal symmetry - see below). On the right the spatial distribution of the $4f$ electrons for the respective $|J_z\rangle$ states.

strongly absorbing for neutrons, and it is also element specific, so that the presence of more than one type of magnetic ion is no limitation.

Over the last 20 years soft-XAS has developed into a powerful technique for studying the element-specific local electronic structure of $3d$ transition metal and $4f$ rare earth compounds. The respective $2p$ -to- $3d$ ($L_{2,3}$) and $3d$ -to- $4f$ ($M_{4,5}$) absorption processes can be well understood in terms of atomic-like transitions into multiplet-split final states [25, 26, 27, 28]. Unique is that the dipole selection rules are very effective in determining which of those final states can be reached and with what intensity for a given initial state symmetry. This makes the technique an extremely sensitive local probe, ideal to study the valence, spin and orbital state of the ions of interest.

The majority of the soft-XAS studies on rare earth materials were so far focused on issues concerning their magnetism by measuring the magnetic circular dichroic effect [29]. Surprisingly, only little attention had been paid on orbital symmetry or crystal-field issues in rare earths: there are a few soft-XAS reports early on addressing surface and interface crystal-fields [30, 31, 32]. As far as bulk materials are concerned, only the giant crystal-field system CeRh_3B_2 has been investigated [33, 34, 35, 36, 37], thereby giving the impression that it would be difficult to study experimentally systems with smaller crystal-fields. Actually, CeRh_3B_2 is a quite special case since the large size of the crystal-field splitting is comparable to that of the spin-orbit interaction, resulting in an intermixing of the $J=7/2$ and $J=5/2$ orbital states [38]. Here we follow up on the theoretical work of Jo *et al.* [33, 34] and show that for the small crystal-fields in rare earth systems a simple mapping can be found between the ground state orbital symmetry and the polarization dependence of the spectra, allowing an accurate and quick quantita-

tive analysis.

The spin orbit interaction in the f shell of rare earth compounds is much larger than the crystal-field splitting due to its small spatial distribution. J in the LS coupling is therefore a good quantum number, and the eigenstates in the presence of crystal-fields can be expressed in terms of linear combinations of the corresponding $|J_z\rangle$ states. In the case of Ce^{3+} with f^1 in tetragonal site symmetry, for example, the 6-fold degenerate $J=5/2$ state splits into three doublets: $|1\rangle = a|\pm 5/2\rangle - b|\mp 3/2\rangle$, $|2\rangle = |\pm 1/2\rangle$ and $|3\rangle = b|\pm 5/2\rangle + a|\mp 3/2\rangle$ with $|\Gamma_7^1\rangle$, $|\Gamma_6\rangle$, and $|\Gamma_7^2\rangle$ symmetry, respectively. The crucial question is which one of these states forms the ground state and what are the a and b coefficients ($a^2+b^2=1$), thus defining the actual charge distribution. In Stevens formalism [39] the tetragonal crystal-field potential of an f^1 is given by the three crystal-field parameters B_2^0 , B_4^0 and B_4^4 , and can be expressed alternatively through the transition energies ΔE_{12} and ΔE_{13} , and the coefficient a .

To study the sensitivity of the $\text{Ce } M_{4,5}$ spectra to the $4f$ charge distribution of the ground state, we performed atomic calculations which include the full multiplet theory [25, 26, 27, 28, 29] using the XTLS 8.3 program [26]. It accounts for the intra-atomic $4f$ - $4f$ and $3d$ - $4f$ Coulomb and exchange interactions, the $3d$ and $4f$ spin-orbit couplings, and the local crystal-field parameters. All atomic parameters were given by the Hartree-Fock values, with a reduction of about 35% for the $4f$ - $4f$ parameters and 25% for the $3d$ - $4f$ to reproduce best the experimental isotropic spectra of Ce materials with low Kondo temperatures, as to account for configuration interaction effects not included in the Hartree-Fock scheme [26].

We start with calculating the $M_{4,5}$ spectra for the pure $|J_z\rangle$ states of the Ce^{3+} with $4f^1$ and $J=5/2$ for two polarizations of the electric field vector \vec{E} , namely $\vec{E} \parallel \mathbf{c}$ and $\vec{E} \perp \mathbf{c}$, where the tetragonal \mathbf{c} -axis is aligned along the \mathbf{z} direction. Fig. 1 shows the results of these calculations. The spectra are dominated by the Ce $3d$ core-hole spin-orbit coupling which splits the spectrum roughly in two parts, namely the M_5 ($h\nu \approx 877 - 887$ eV) and M_4 ($h\nu \approx 895 - 905$ eV) white lines regions. Crucial is that there is a strong polarization dependence which is characteristic for each of the states. The existence of such a polarization dependence is intuitively clear when looking at the spatial distributions of the f electrons of the respective $|J_z\rangle$ states as shown also in Fig.1: the distributions differ remarkably between the different $|J_z\rangle$ states.

The results in Fig.1 are a nice demonstration of the so-called initial state symmetry effect, an important concept for the determination of the ground state orbital symmetry in real materials: the splitting between the various crystal-field states can be small, e.g. smaller than the broadening of the spectra due to lifetime, phonon or experimental resolution, and yet the polarization depen-

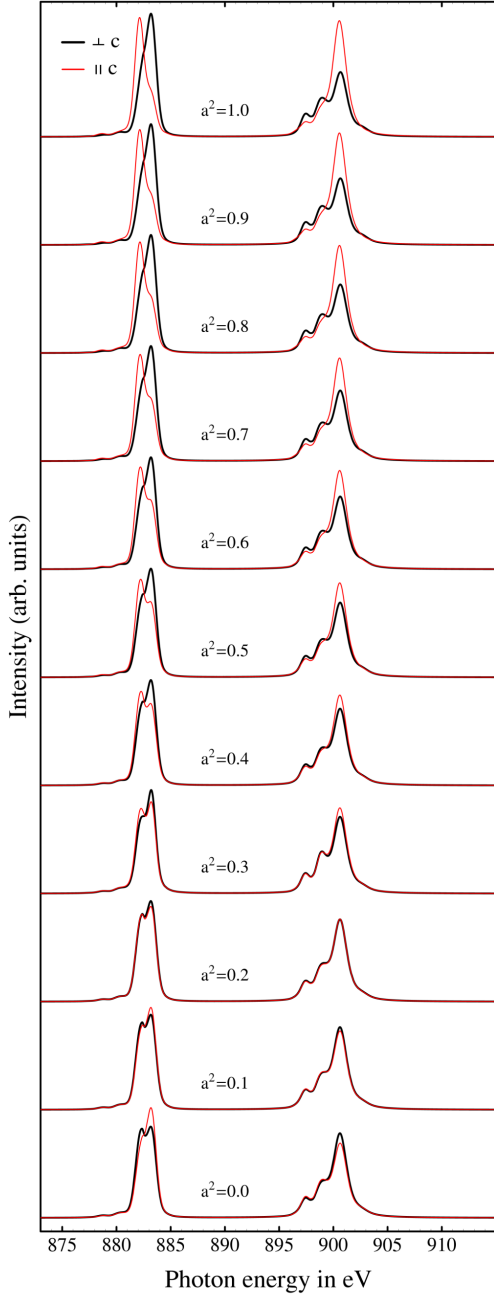


FIG. 2: (color online) Top: Calculated $M_{4,5}$ soft-x-ray absorption spectra for the mixed states $a|\pm 5/2\rangle - b|\mp 3/2\rangle$ for mixing factors a^2 from 0 to 1 for light polarized \parallel and \perp c .

dence can be very large. Important is that the temperature is sufficiently low so that primarily only the lowest state is populated and contributes to the signal. In fact, we can make use of the fact that the crystal-field splittings in rare earth materials are typically much smaller than the ≈ 400 meV spectral broadening. When calculating the polarization dependence of the states $|1\rangle$ or $|3\rangle$, we find they can be well approximated by an incoherent sum of the $|3/2\rangle$ and $|5/2\rangle$ spectra, weighted with

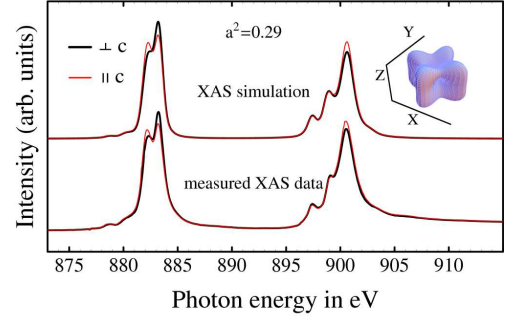


FIG. 3: (color online) Bottom: experimental $M_{4,5}$ soft-x-ray absorption spectra of CePd_2Si_2 at $T = 50$ K for light polarized \parallel and \perp c . Top: simulated $M_{4,5}$ spectra with $a^2 = 0.29$.

the proper a^2 and b^2 parameters. The results are shown in Fig. 2, where we let a^2 run from 0 to 1, with $a^2=0$ corresponding to a pure $|3/2\rangle$ and $a^2=1$ to a pure $|5/2\rangle$ state. Fig. 2 in effect can serve as a map to find the coefficient a^2 directly from an experiment. It should be generally applicable for tetragonal Ce materials without the need to know the crystal-field splittings themselves as long as the total crystal-field splitting is small in comparison to the spin orbit splitting of 230 meV. Yet, having knowledge of the crystal-field energies e.g. from neutron scattering, this XAS technique will also enable us to give a clear and unique set of crystal-field parameters, independent of molecular fields. Important is, of course, that this atomic approach is only accurate for materials in which the Kondo temperature is sufficiently smaller than the splitting between the lowest and first excited crystal-field state, otherwise the analysis needs to be extended by using the Anderson impurity model.

We have chosen to measure the linear polarized soft-XAS spectra of CePd_2Si_2 in order to proof the feasibility of the technique. Several groups measured the crystal-fields scheme of CePd_2Si_2 with neutron scattering [19, 20, 40, 41] and agree in the energy splitting but end up with considerably different ground state wave functions. The authors of [19] and [20] both took the energy splitting from neutron data and fitted the single crystal static susceptibility in order to obtain the ground state wave function. Both groups obtained decent fits although different ground state coefficients were assumed. This is due to the fact that anisotropic molecular field parameters were introduced in order to take into account the antiferromagnetic order at 10 K, ending up with too many free parameters for a unique fit. The CePd_2Si_2 single crystal used was grown by the Czochralski method as described in [19]. It orders at $T_N \approx 10$ K. The XAS measurements were performed at the Dragon beamline of the NSRRC in Taiwan. The spectra were recorded using the total electron yield method in an ultra-high-vacuum chamber with a base pressure of 2×10^{-10} mbar. Clean

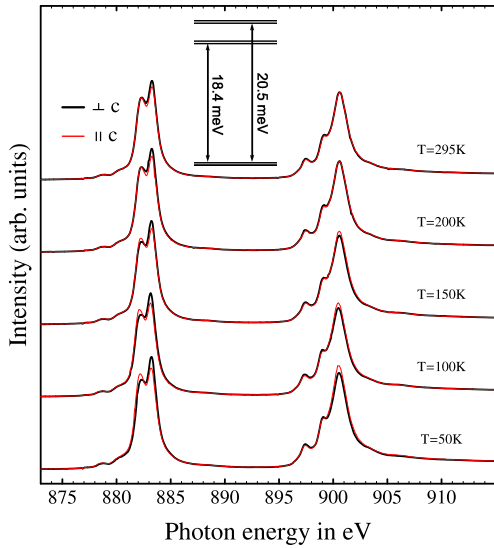


FIG. 4: (color online) Temperature dependence of the experimental $M_{4,5}$ soft-x-ray absorption spectra of CePd_2Si_2 . The inset gives the crystal-field transition energies as in [40]

sample areas were obtained by cleaving the crystals *in-situ*. The photon energy resolution at the Ce $M_{4,5}$ edges ($h\nu \approx 875 - 910$ eV) was set at 0.4 eV, and the degree of linear polarization was $\approx 98\%$. The CePd_2Si_2 single crystal was mounted with the **c**-axis perpendicular to the Poynting vector of the light. By rotating the sample around this Poynting vector, the polarization of the electric field vector can be varied continuously from $\vec{E} \parallel \mathbf{c}$ to $\vec{E} \perp \mathbf{c}$. This measurement geometry allows for an optical path of the incoming beam which is independent of the polarization, guaranteeing a reliable comparison of the spectral line shapes as a function of polarization.

The bottom curves of Fig. 3 show the measured soft-XAS spectra of CePd_2Si_2 at $T = 50$ K for the light polarized parallel and perpendicular to the **c**-axis. The spectral features are well resolved and their sharpness can be taken as a confirmation for the atomic character of the Ce states. Important is that there is a polarization dependence and that this can be clearly seen due to the excellent signal-to-noise/background ratio. Comparing these experimental spectra to the simulations in Figs. 1 and 2, one can immediately deduce that the ground state must be state $|1\rangle$ with a^2 close to 0.3. Indeed, a more detailed simulation analysis yields the best fit for $a^2=0.29$. We know from neutron data [40, 41] that the first excited crystal-field level is above 18 meV, i.e. well above 200 K, so that at $T = 50$ K only the ground state contributes to the spectra. When simulating the data the Boltzmann factor was nevertheless taken into account. The value found for a^2 corresponds to $a=0.54$ and $b=0.84$, so that we essentially confirm the ground state of CePd_2Si_2 as proposed by [19]: $|1\rangle = 0.55 |\pm 5/2\rangle - 0.84 |\pm 3/2\rangle$. The corresponding spatial distribution of the 4f electron in

this ground state is shown in the inset of Fig. 3.

To confirm the crystal-field nature of the polarization effect, we have also carried out measurements at elevated temperatures. The polarization dependence in the spectra diminishes as the temperature rises as is shown in Fig. 4 for 50, 100, 150, 200 and 295 K. This is in accordance with the increased population of higher crystal-field levels, resulting eventually in an isotropic spectrum at sufficiently high temperatures. These elevated temperature spectra can be well described using the ground state symmetry and coefficient from the 50 K spectrum and the crystal-field energies from neutron data [40], depicted in the inset of Fig. 4. One only has to take into account the Boltzmann factor for each respective temperature.

In conclusion we have shown that the Ce $M_{4,5}$ spectra have a polarization dependence which is characteristic for the charge distribution of the Ce 4f states. We have provided a set of reference spectra (Figs. 1 and 2) from which one can find the ground state parameters directly from the experiment, without the need to know the crystal-field energies themselves as long as they are small. Using this method we have investigated the local electronic structure CePd_2Si_2 and settled the debate concerning the ground state wave function of this compound, demonstrating that soft-x-ray absorption spectroscopy is a powerful method complementing neutron scattering.

We would like to thank Lucie Hamdan for her skillful assistance in preparing the experiments, and John Mydosh and Daniel Khomskii for valuable discussions.

-
- [1] D. Jaccard, K. Behnia, and J. Sierro, Phys. Lett. A **165**, 475 (1992).
 - [2] R. Movshovich *et al.*, Phys. Rev. B **53**, 8241 (1996).
 - [3] N. D. Mathur *et al.*, Nature **394**, 39 (1998).
 - [4] H. Hegger *et al.*, Phys. Rev. Lett. **84**, 4986 (2000).
 - [5] R. Movshovich *et al.*, Phys. Rev. Lett. **86**, 5152 (2001).
 - [6] T. Park *et al.*, Nature **440**, 65-68 (2006).
 - [7] O. Trovarelli *et al.*, Phys. Rev. Lett. **85**, 626 (2000).
 - [8] H. v. Löneysen, A. Rosch, M. Vojta, and P. Wölfle, Cond. Mat. /0606317v2; Rev. Mod. Phys. (in press) and references therein.
 - [9] P.G. Pagliuso *et al.*, Physica B **320**, 370 (2002).
 - [10] F. P. Mena, D. van der Marel, and J. L. Sarrao, Phys. Rev. B **72**, 045119 (2005).
 - [11] K. S. Burch *et al.*, Phys. Rev. B **75**, 054523 (2007).
 - [12] P. Ghaemi and T. Senthil, Phys. Rev. B **75**, 144412 (2007).
 - [13] G. Zwircknagl in Adv. Phys. **41** No. 3, 203-302 (1992).
 - [14] P. Fazekas, *Lecture Notes on Electronic Correlation and Magnetism* (World Scientific Singapore, 1999)
 - [15] A. Kiss and P. Fazekas, J. Phys. Cond. Mat. **15**, 2109 (2003)
 - [16] H.N. Kono, K. Kubo, and Y. Kuramoto, J. Phys. Soc. Jpn. **73**, 2948 (2004)
 - [17] Y. Kuramoto, J. Otsuki, A. Kiss, and H. Kusunose, J. Phys. Soc. Jpn. **75** Suppl., 209 (2006)

- [18] E.A. Goremychkin and R. Osborn, Phys. Rev. B **47**, 14280 (1993).
- [19] N. H. van Dijk *et al.*, Phys. Rev. B **61**, 8922 (2000).
- [20] H. Abe *et al.*, J. Mag. Mag. Mat. **177-181**, 479 (1998).
- [21] U. Witte, R. Schedler, O. Stockert, and M. Loewenhaupt, J. Low Temp. Physics **147** No 314, 97 (2007).
- [22] B. Janoušová, J. Kulda, M. Diviš, and V. Sechovský, Phys. Rev. B **69**, 220412 (2004).
- [23] J. X. Boucherle and J. Schweizer, Physica **B** and **C** **130**, 337 (1985).
- [24] J. X. Boucherle *et al.*, J. Phys. Cond. Mat. **13**, 10901 (2001).
- [25] B. T. Thole *et al.*, Phys. Rev. B **32**, 5107 (1985).
- [26] A. Tanaka and T. Jo, J. Phys. Soc. Jpn. **63**, 2788 (1994).
- [27] F. M. F. de Groot, J. Electron Spectrosc. Relat. Phenom. **67**, 529 (1994).
- [28] Theo Thole Memorial Issue, J. Electron Spectrosc. Relat. Phenom. **86**, 1 (1997).
- [29] J. B. Goedkoop *et al.*, Phys. Rev. B **37**, 2086 (1988).
- [30] M. Sacchi, O. Sakho, and G. Rossi, Phys. Rev. B **43**, 1276 (1991).
- [31] R. J. H. Kappert, J. Vogel, M. Sacchi, and J. C. Fuggle, Phys. Rev. B **48**, 2711 (1993).
- [32] P. Castrucci *et al.*, Phys. Rev. B **52**, 14035 (1995).
- [33] T. Jo, Prog. Theor. Phys. Suppl. **101**, 303 (1990).
- [34] T. Jo and S. Imada, J. Phys. Soc. Jpn. **59**, 2312 (1990).
- [35] K. Yamaguchi *et al.*, Phys. Rev. B **46**, 9845 (1992).
- [36] S. Nakai *et al.*, Phys. B **186**, 74 (1993).
- [37] K. Yamaguchi *et al.*, Phys. Rev. B **51**, 13952 (1995).
- [38] F. Givord, J.-X. Boucherle, E. Lelièvre-Berna, and P. Lejay, J. Phys. Cond. Mat. **16**, 1211 (2004).
- [39] K.W. H. Stevens, Proc. Phys. Soc. A **65**, 209 (1951).
- [40] A. Severing *et al.*, Phys. Rev. B **39**, 2557 (1989).
- [41] R. A. Steeman *et al.*, J. Appl. Phys. **67** 5203 (1990) .